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Effect of substrate misorientation on tear-drop-like hillock defect densities in InP and GaInAsP grown by metalorganic chemical vapor deposition

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Tear-drop-like hillock (TLH) defects in InP and GaInAsP layers grown by MOCVD have been systematically studied. It was found that the formation of TLH defects is caused both by dislocations and by substrate orientations. There is a critical misorientation angle for the appearance of TLH defects. TLH defects disappear above the critical angle. The angle, which is changed by the growth rate and the growth temperature, is 0.06° when the growth rate is 1 μm/h and the growth temperature is 625°C. When the angle is 0.25°, terraces appear on the surface of epitaxial layers. By using substrates with appropriate misorientation angles, smooth surfaces without any TLH defects or terraces could be obtained.

1. Introduction

Epitaxial layers such as GaInAsP and GaInAs on InP substrates are important materials for long wavelength optical devices (laser diodes, light emitting diodes, and photodiodes) and for high frequency devices (high electron mobility transistors, heterostructure bipolar transistors). The MOCVD growth method is being industrially used for their fabrication. Control of the morphology of the epitaxial layers grown by MOCVD is therefore becoming increasingly important.

It is well known that tear-drop-like hillock (TLH) defects are formed on InP epitaxial layers grown by MOCVD. It was difficult to control their densities since the formation mechanism is not clear. The fact that they are formed depending on the InP substrate lots suggests that they are due to substrate preparation. Even though the reduction of hillock densities is indispensable for the morphology control of the epitaxial layers, there were few reports discussing the mechanism of the formation of these TLH defects. In the case of AlGaAs epitaxial layers on GaAs grown by MOCVD, Johnston and Legg [1] showed that the substrate misorientation affected these hillock defect densities. In their experiments, they used substrates whose misorientation angle was of the order of 1°. Hamada et al. [2] reported that the hillock defects in GaInP epitaxial layers grown on the (100) plane of GaAs substrates were caused by Ga droplets. These defects disappeared when the substrate misorientation was over 5° toward ⟨011⟩. Hirano et al. [3] reported the formation of TLH defects in InP epitaxial layers. By using $(100) \pm 0.03°$ oriented InP substrates, they showed that TLH defect densities are related to dislocation densities, and they decrease as dislocation densities reduce. It was not, however, found how the substrate misorientation of InP substrates affected TLH defect densities.

For InP substrates, there are two types of InP materials. One consists of those which are doped with S or Zn and which have very low dislocation

Table 1
Substrates and growth conditions used for MOCVD growth

Run No.	Growth conditions					Substrate			
	Structure	Thickness (μm)	Temperture (°C)	Growth rate (μm/h)	V/III	Dopant	Misorientation angle (mean value, degrees)	EPD (cm^{-2})	Remarks
1	GaInAsP/InP	1.0	700	1.0	250	Sn	0.030	30000	
						Sn	0.030	10000	
2	GaInAsP/InP	1.0	720	1.0	250	Fe	0.014	16000	
3	InP	4.0	625	1.0	250	Fe	0.014	16000	Fig. 1a
4	InP	1.0	625	1.0	250	Fe	0.014	16000	Figs. 1b, 2
5	InP	1.0	625	0.3	750	Sn	0.041	40000	Fig. 8a
						Sn	0.083	30000	
						Sn	0.056	10000	
6	InP	1.0	700	1.0	250	Sn	0.041	40000	Fig. 6c
						Sn	0.083	30000	
						Sn	0.056	10000	
7	InP	1.0	625	1.0	250	Sn	0.041	40000	Figs. 6b, 8b
						Sn	0.083	30000	
						Sn	0.056	10000	
8	InP	1.0	580	1.0	250	Sn	0.081	30000	Fig. 8a
						Sn	0.056	10000	
9	InP	1.0	625	2.0	125	Sn	0.081	30000	Fig. 8c
						Sn	0.056	10000	
10	InP	1.0	700	0.3	750	Sn	0.034	66000	
						Sn	0.056	10000	
11	InP	1.0	720	1.0	250	Sn	0.034	66000	
						Fe	0.024	30000	
						Sn	0.056	10000	

densities (lower than several thousand cm^{-2}) due to impurity hardening [3]. The other consists of those which are doped with Fe or Sn and which have dislocation densities in the range of (0.8–3) $\times 10^4$ cm^{-2}. If TLH defects are formed a priori due to dislocations, they cannot be eliminated if Fe-doped or Sn-doped substrates are used for epitaxial growth.

In the present work, we made a systematic study to clarify the effect of substrate misorientation and that of growth conditions, such as growth rate and growth temperature, on the TLH defect formation for InP and GaInAsP epitaxial growth by MOCVD. From these investigations, we have tried to find optimum growth conditions under which TLH defects can be eliminated even when using Fe- or Sn-doped substrates.

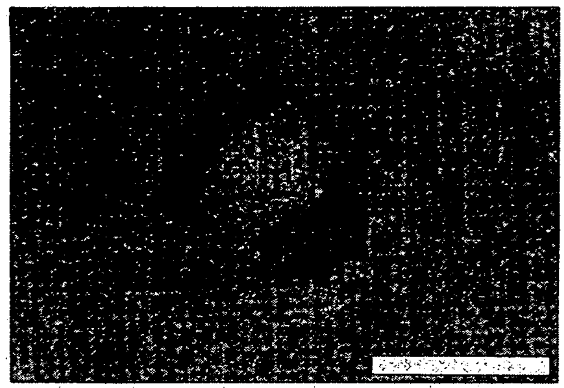

Fig. 2. TLH defect after Huber etching. Marker represents 50 μm.

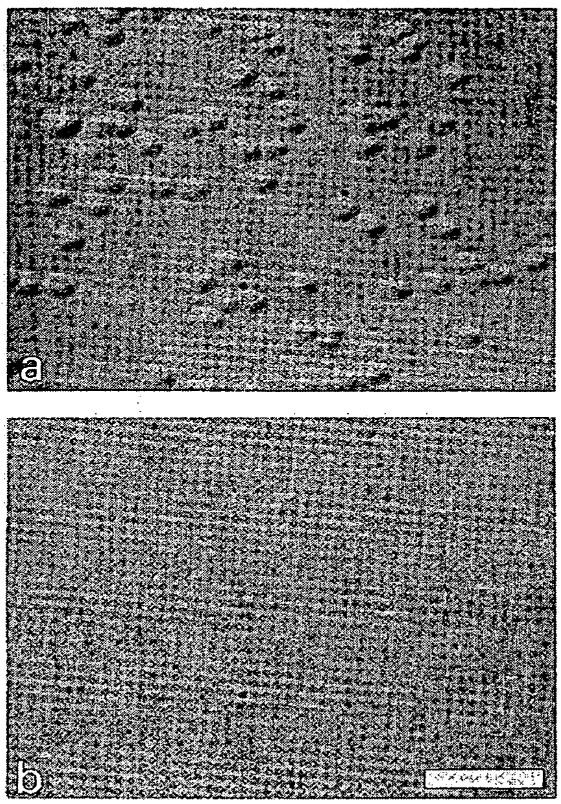

Fig. 1. TLH defects on InP layers grown by MOCVD using Fe doped substrates: (a) 4 μm thick and (b) 1 μm thick epitaxial layer. Marker represents 200 μm.

2. Experiment

Fe- and Sn-doped substrates slightly misoriented from (100), whose dislocation densities are of the order of 10^4 cm^{-2}, were used for the present experiments. In order to examine the effect of misorientation, various substrates were used whose misorientation angles ranged from

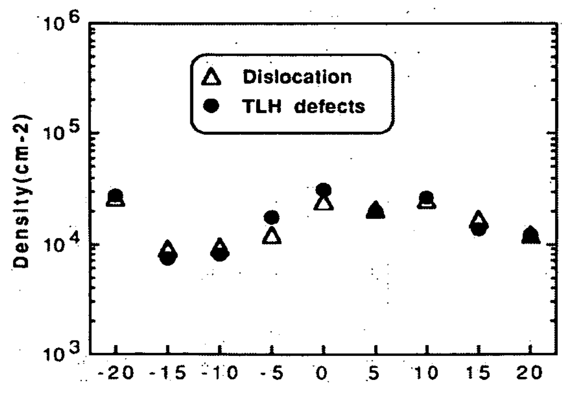

Fig. 3. TLH defect densities and dislocation densities on a Sn-doped substrate with misorientation angle of 0.03°.

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0.005° to 0.25° toward $\langle 0\bar{1}1\rangle$ and $\langle 0\bar{1}\bar{1}\rangle$. Undoped InP and undoped $Ga_xIn_{1-x}As_yP_{1-y}$ ($x = 0.28$, $y = 0.61$) epitaxial layers, whose thickness was between 1 and 4 μm, were grown by MOCVD. The growth was carried out at 76 Torr in a vertical multi-wafer reactor. Source materials were trimethylindium (TMI), trimethylgallium (TEG), phosphine (PH_3), and arsine (AsH_3). The total flow rate was 10 l/min. The growth temperature was from 580 to 700°C and the growth rate was from 0.3 to 2.0 μm/h. The PH_3 pressure was 3.1 Torr. V/III ratios were from 125 to 750. In

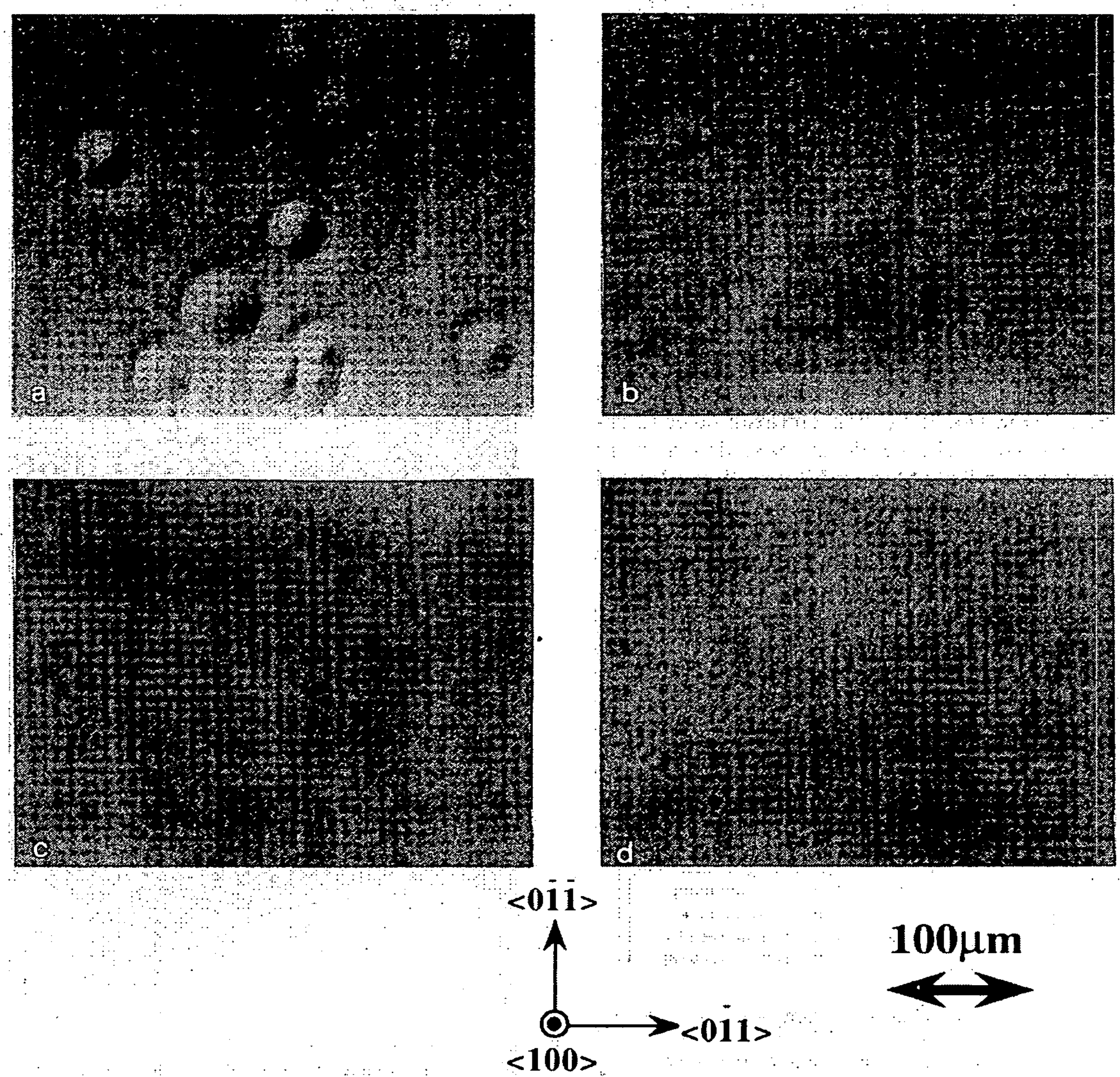

Fig. 4. Nomarski micrographs of InP epitaxial layers using Sn-doped InP substrates with various misorientations: (a) 0.005° off; (b) 0.03° off; (c) 0.07° off; (d) 0.25° off. Off-angle direction is toward $\langle 0\bar{1}1\rangle$.

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table 1, the present experimental conditions such as growth temperature, growth rate and misorientation angle of the substrates are summarized. Misorientation angles were measured by a cut-face detection apparatus (Rigaku Co. Ltd., Model 2992G1) based on the X-ray diffraction method. The heights of the TLH defects were determined by a Taly Step. Huber etchant ($HBr:H_3PO_4 = 1:2$ at room temperature) was used for measuring the dislocation densities.

3. Experimental results

3.1. Relationship between TLH defects and dislocations

Fig. 1 shows a photograph of TLH defects on undoped InP epitaxial layers grown by MOCVD using Fe-doped substrates (runs No. 3 and No. 4 in table 1). Their diameters were 80 μm (4 μm thick, fig. 1a) and 20 μm (1 μm thick, fig. 1b). They became smaller as the epitaxial layer thickness decreased. The height of these defects were measured by a Taly Step and it was 10 nm for a 4 μm thick epitaxial layer.

Fig. 2 shows a TLH defect after Huber etching. The etching was carried out for the undoped InP epitaxial layer with the thickness of 4 μm. It was found that etch pits were clearly revealed at the top of each TLH defect. Since dislocations

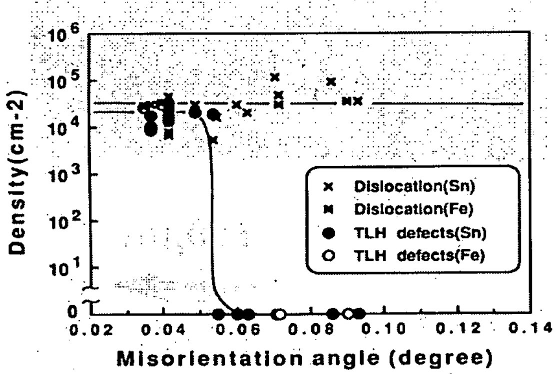

Fig. 5. Dependence of TLH defect densities in InP epitaxial layers on the misorientation angle (625°C, 1 $\mu m/h$).

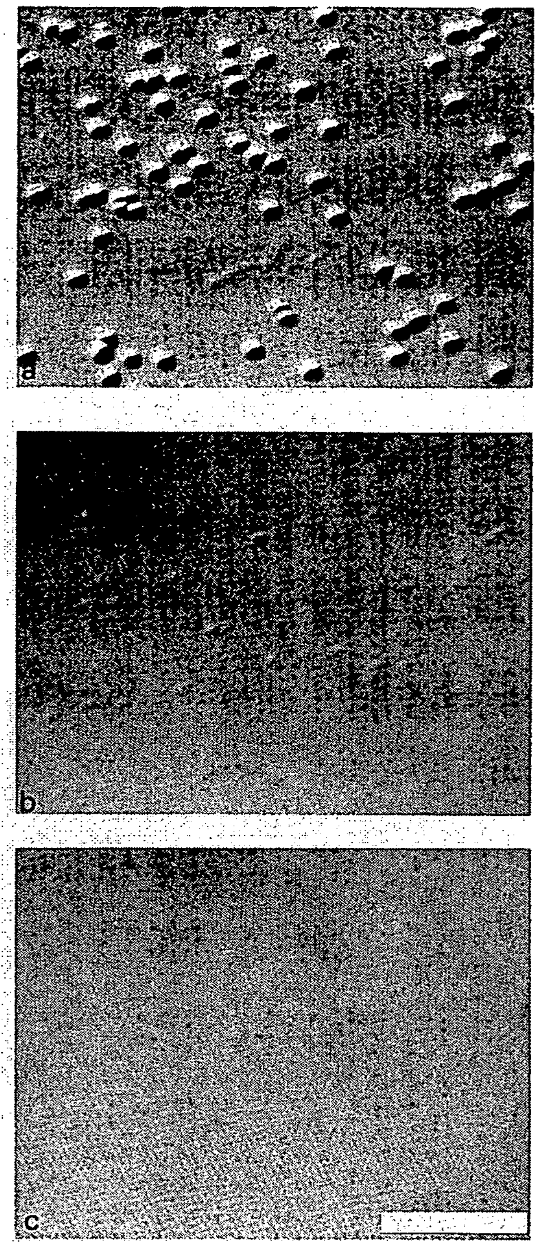

Fig. 6. Nomarski micrographs of InP epitaxial layers on 0.05° misorientated Sn-doped InP substrates (the growth rate is 1 $\mu m/h$): (a) 580°C; (b) 625°C; (c) 700°C. Marker represents 200 μm.

are known to be revealed as etch pits by Huber etching, these observations suggest that TLH defects are generated from the intersection between the surface and a dislocation, and grow during epitaxial growth.

Fig. 3 shows the comparison of TLH defect densities with the dislocation densities over a Sn-doped substrate whose mean misorientation angle was 0.03°. The measurement was carried out at each point of a 5 mm grid. The TLH defect densities and the dislocation densities were nearly equal at every measured point. These results are in good agreement with those previously reported for Sn-doped substrates [3].

3.2. Effect of substrate misorientation

Fig. 4 shows the dependence of the TLH defect shapes on the orientation of Sn-doped substrates (runs No. 3 and No. 5 in table 1). The direction of the misorientation was toward $\langle 0\bar{1}1 \rangle$. TLH defects had round shapes when the misorientation angles were 0.0005° (fig. 4a). When the angles became larger, TLH defects showed oval shapes like tear drops with their tail direction having the direction of the misorientation (fig. 4b). When the angle was over 0.06°, no TLH defects were observed on the surface (fig. 4c). This suggests that there is a critical misorientation angle at which TLH defects disappear. Even

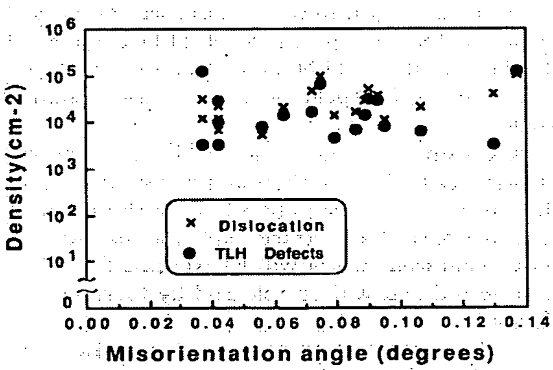

Fig. 7. Dependence of TLH defect densities in InP epitaxial layers on the misorientation angle (580°C, 1 μm/h).

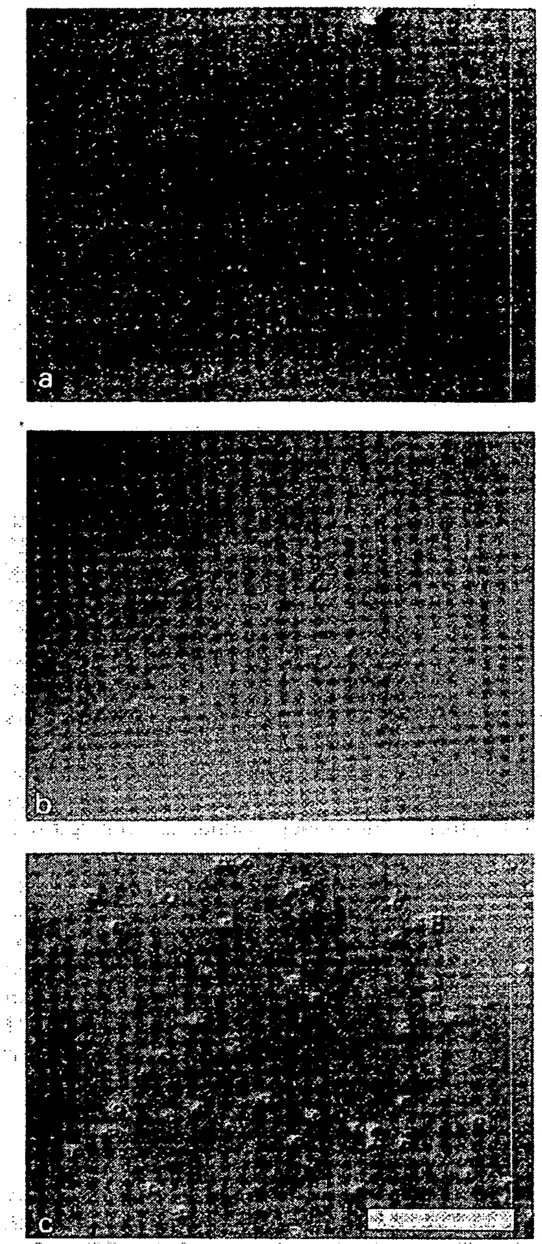

Fig. 8. Nomarski micrographs of InP epitaxial layers on 0.05° misorientated Sn-doped InP substrates (the growth temperature is 625°C).

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TLH defect and dislocation densities, and Mr. K. Nakaya for measuring misorientation angles.

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